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Formulation and implementation of the relativistic Fock-space coupled cluster method for molecules

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An implementation of the relativistic multireference Fock-space coupled cluster method is presented which allows simultaneous calculation of potential surfaces for different oxidation states and electronic levels of a molecule, yielding values for spectroscopic constants and transition energies. The method is tested in pilot calculations on the I_2 and HgH molecules, and is shown to give a good and balanced description of various electronic states and energies. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415746]

I. INTRODUCTION

The relativistic coupled cluster (RCC) method for two- and four-component molecular wave functions has recently been implemented[1] in the MOLFDIR[2] program system and applied to several molecules.[3] This scheme is applicable in single-reference situations, where the state of interest can be described approximately by a single Slater determinant, which may be closed or open shell. Various flavors of multireference coupled cluster schemes exist,[4] the most widely used being the Fock-space approach.[5,6] The relativistic Fock-space coupled cluster method has been applied in recent years to a large number of atoms, yielding high-accuracy results for a variety of transition energies (ionization potentials, excitation energies, electron affinities).[7] Several applications to molecules have also been performed, using the one-component Douglas–Kroll–Hess approach[8–10] or the four-component Dirac–Coulomb–Breit Hamiltonian.[11,12]

Atomic applications enjoy the advantage of spherical symmetry, making possible a separation of the angular-spin variables, amenable to analytic integration, from the radial functions, which are integrated numerically or expanded in a basis. The angular momentum methods needed for integrating over angular and spin variables are well known.[5] They make the computational implementation of the RCC method somewhat cumbersome and less straightforward, as radial integrals have to be multiplied by factors arising from angular-spin integrations. In particular, antisymmetrized quantities, used routinely in molecular coupled cluster programs, are not suitable for spherical implementations, as the direct and exchange radial quantities are in general multiplied by different angular-spin factors. This is more than compensated by the need to solve only radial equations, making it possible to use very large basis sets and correlate many electrons (a recent calculation of element 114 levels[13] used a $35s30p21d16f11g9h9i7k7l$ basis and correlated 36 electrons).

Here we describe the implementation of the Fock-space coupled cluster method in the one-hole and one-particle sectors in the MOLFDIR[2] and DIRAC[14] program systems. The basic procedures are similar to those described earlier[1] for the single-reference scheme, and only the new features will be given in detail. Pilot applications to the I_2 and HgH molecules are presented. The aim of these calculations is to demonstrate the features and feasibility of the method rather than provide definitive potential functions or spectroscopic constants, and basis sets of moderate size are therefore used.

II. THEORY

A. Relativistic Fock-space coupled cluster method

The starting point of the method is the Dirac–Coulomb(–Gaunt) Hamiltonian in the no-pair approximation, which may be written in second quantized form as

$$\hat{H}=\sum_{P,Q} Z_Q^P \hat{E}_P^Q+\frac{1}{4}\sum_{P,Q,R,S} V_{RS}^{PQ}\hat{E}_{PQ}^{RS}. \tag{1}$$

Here $Z_Q^P=\langle Q|h|P\rangle$ is the one-electron integral, $V_{RS}^{PQ}=\langle RS||PQ\rangle$ is the antisymmetrized two-electron interaction, $\hat{E}_P^Q$ and $\hat{E}_{PQ}^{RS}$ are the replacement operators defined by Paldus.[15] The no-pair Hamiltonian (1) has the same form as the nonrelativistic Schrödinger operator, differing only in the definition of the integrals Z and V. This leads to straightforward extension of the nonrelativistic coupled cluster method to relativistic closed-shell[16] and open-shell[17] implementations. Here we address the multireference valence-universal Fock-space method. The equations determining the T excitation amplitudes in a complete model space P may be derived from the cluster equation[5]

$$[\hat{T},\hat{H}_0]=\hat{Q}(V\hat{\Omega}-\hat{\Omega}\hat{H}_{\text{eff}})_{\text{conn}}\hat{P}, \tag{2}$$

$$\hat{H}_{\text{eff}}=\hat{P}\hat{H}\hat{\Omega}\hat{P}, \tag{3}$$

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where $\hat{P}$ and $\hat{Q}$ are the usual projection operators, and $\hat{\Omega} = \{\exp \hat{T}\}$ is the normal-ordered wave operator.

The Fock-space excitation operator $\hat{T}$ is defined with respect to a reference determinant, which we take to be closed shell (this restriction makes application more convenient, but a single open-shell determinant may also be employed). In addition to the usual decomposition into terms with different total (l) number of excited electrons, $\hat{T}$ is partitioned according to the number of valence holes (m) and valence particles (n) with respect to the reference determinant,

$$\hat{T} = \sum_{m \geqslant 0} \sum_{n \geqslant 0} \left(\sum_{l} \hat{T}_l^{(m,n)} \right). \tag{4}$$

The coupled cluster equations can be solved hierarchically, since equations for $\hat{T}$ in a given sector, $\hat{T}^{(m,n)}$, do not involve amplitudes from higher sectors. After convergence is achieved in a particular sector, $\hat{H}_{\text{eff}}$ is diagonalized to yield all energies of $P^{(m,n)}$ states in that sector relative to the correlated energy of the reference determinant. Thus, a large number of states may be obtained simultaneously. This is an advantage over the single reference approach which requires a costly four-component Hartree–Fock and four-index transformation step prior to the calculation of each CC energy. An added advantage of the method is that full spatial and spin symmetry is built in by including all relevant determinants in P, avoiding symmetry breaking which may occur in single-determinant open-shell approaches.[18] All calculations reported here are at the Fock-space coupled cluster singles and doubles (FSCCSD) level.

B. Implementation notes

The first stage in applying the Fock-space CC method involves solving the equations in the (0,0) sector. This is the usual single-reference problem; its implementation in the framework of two- and four-component relativistic functions has been described in Ref. 1. Here the extension to the one-hole and one-particle sectors will be delineated, using the notations and equations of the previous publication[1] and listing the changes and additions required. Details will be given about the one-particle sector; the scheme for the one-hole sector is similar and can be derived by analogy. Equation (n) of Ref. 1 will be denoted as Eq. (VLD-n).

The space $P^{(0,1)}$ is defined by designating selected virtual spinors as *active virtuals*; $P^{(0,1)}$ comprises all determinants with one electron added to the reference determinant in an active virtual spinor. Adopting the labeling[1] of occupied spinors by I, J, K, L and virtual spinors by A, B, C, D, active virtual spinors will be labeled by E,F and inactive ones by V, W. The working equations for determining $\hat{T}^{(0,1)}$ cluster amplitudes are (VLD-4)–(VLD-16), modified as follows:

(1) All terms in (VLD-4) and (VLD-5) have, after summations are carried out, the general form X_I^A and X_{IJ}^{AB}, respectively, corresponding to one- or two-electron excitations in the (0,0) sector. Here the relevant indices are changed so that the resulting terms will have the form X_E^V and X_{EJ}^{AB}, corresponding to $P \rightarrow Q$ transitions in the (0,1) sector. The summation indices are not affected.

(2) New diagrams, resulting from the second term on the right-hand side of Eq. (2), will be added in Eqs. (VLD-4) and (VLD-5). These are Brandow's[19] "folded diagrams," which appear in multireference many-body methods. The modified equation (VLD-4), with the indices I and A replaced by E and V, respectively, is augmented by the term $-\Sigma_F T_F^V (H_{\text{eff}})_E^F$, while the two-body equation (VLD-5), with the index I replaced by E, includes the new term $-P_{AB} \Sigma_F T_{FJ}^{AB} (H_{\text{eff}})_E^F$, where the permutation operator P_{AB} is defined in (VLD-6).

(3) Elements of the $\hat{H}_{\text{eff}}$ matrix occur in the new diagrams described in item 2 and in Eq. (3). They have the same form as the amplitudes $T_E^V (F_E^E - F_V^V)$ prior to addition of the folded diagrams. Diagonalization of this effective Hamiltonian yields the electron affinities of the system described by the reference determinant.

The implementation was performed striving to minimize the modifications to the existing single reference code,[1] which is based on using efficient and parallelized matrix–matrix operations. The two arrays of dimension $N_v N_o$ and $1/4\ N_v^2 N_o^2$ used to store the T_1 and T_2 amplitudes were extended to hold $(N_v + N_{\text{ao}})(N_o + N_{\text{av}})$ and $1/4\ (N_v + N_{\text{ao}})^2 (N_o + N_{\text{av}})^2$ elements (the various N values denote the numbers of occupied, virtual, active occupied or active virtual orbitals). This allows simultaneous storage of amplitudes and effective Hamiltonian matrix elements of all sectors of Fock space up to the two-hole two-particle sector. In this manner, only one set of (parallelized) computational kernels needs to be called for all sectors, making the code easy to maintain and improve.

Having all amplitudes available at the same time, we could in principle solve the equations for all sectors of the Fock space simultaneously. This computationally attractive scheme makes convergence more difficult, and we decided to stick to the conventional scheme and solve the equations sector by sector. The resulting additional work may be reduced, without loss of computational efficiency, by skipping recalculation of the converged amplitudes that belong to lower sectors of the Fock space, but this was not necessary in the calculations done so far. The time spent in the CC part is usually rather small compared to other steps of the relativistic calculation (in particular the four-index transformation required to obtain two-electron integrals over the molecular four spinors). To illustrate the procedure we look in more detail at the modifications made in the evaluation of the T_1 equation (VLD-4) for the one-particle sector.

The T_1 equation is solved iteratively by constructing S_I^A, from which T_I^A will be obtained upon division by $F_I^I - F_A^A$, using T amplitudes from the previous iteration. Extending the ranges of the arrays and calling the standard single reference subroutine then gives the $(H_{\text{eff}})_E^F$ terms and all contributions to T_E^V (except the folded diagrams) as a subset of the complete T_1 array. After this simple generic step, it only remains to add the new terms of the previously mentioned item (2) above to T_E^V, using the available $(H_{\text{eff}})_E^F$ values. When the iterated amplitudes have converged, the H_{eff} ma-

trix is diagonalized to yield the energies associated with the addition of an electron to the reference system. The precise formulas for this sector read

$$S_E^A = F_E^A - 2\sum_{K,C} F_C^K T_K^A T_E^C + \sum_C H_C^A T_E^C - \sum_K H_E^K T_K^A - (F_A - F_E^E) T_E^A + \sum_{K,C} H_C^K (T_{EK}^{AC} + T_K^A T_E^C) + \sum_{K,C} V_{EC}^{AK} T_K^C + \sum_{K,C<D} V_{CD}^{AK} \tau_{EK}^{CD} - \sum_{K<L,C} V_{EC}^{KL} \tau_{KL}^{AC}. \quad (5)$$

The Hamiltonian matrix elements are given as $(H_{\mathrm{eff}})_E^F = S_E^F$, and the iterated amplitudes are obtained as

$$T_E^V = \left(S_E^V - \sum_F (H_{\mathrm{eff}})_E^F T_F^V \right) \Big/ (F_E^E - F_V^V). \quad (6)$$

Equation (VLD-5) for the T_2 amplitudes is solved in a similar manner, except that the effective Hamiltonian matrix elements appearing in the S_2 array belong to the $(0h,2p)$ sector and are not used in the current work.

III. THE I_2 MOLECULE

The I_2 molecule and its anion and cation provide good test cases for the performance of relativistic electronic structure methods, because calculation of their spectroscopic properties requires inclusion of both electron correlation and spin–orbit coupling effects. In this work we concentrate on the ground state of the neutral molecule and the states reached from it by adding or removing one electron. These are all well characterized experimentally, and previous theoretical work may be used for comparison. Since the goal of this paper is to demonstrate the application of the relativistic Fock space method in the context of molecular calculations, no extensive studies of basis set or active space convergence have been carried out. The contracted pVTZ basis set[20] and active space used are identical to the ones used in the earlier calculation of de Jong *et al.*[21] on the same molecule, to facilitate comparison with the single reference CC approach. Thirty-four electrons were correlated, freezing $4p$ and deeper core orbitals, which give insignificant contributions when calculated in this basis. For the same reason, corelike virtuals (with energies above 10 hartree) were excluded from the virtual space. In order to reach quantitative accuracy, the basis should be extended by at least one g function, and probably also functions of higher angular momentum.[22] Such calculations, while feasible on a more powerful computer, will be rather time consuming, and are left for future work. All calculations reported here were run on a PC with 512 Mbytes of memory under Linux.

Our standard approach is to use the four-component Dirac–Coulomb (DC) Hamiltonian, with the contribution of the (SS|SS) class of two-electron integrals estimated by a simple point charge model.[23] This method does not include the effect of spin–spin interactions as contained in the Breit or Gaunt operators. Since these small interactions may have an effect on the calculated potential energy surfaces, we estimate their contribution by comparing Hartree–Fock calculations based on the Dirac–Coulomb and on the full Dirac–Coulomb–Gaunt (DCG) Hamiltonian. The energy difference between the two sets of calculations gives the magnitude of the Gaunt energy correction as a function of bond distance. This slowly varying function was fitted to a fourth-order polynomial and added to the potential energy obtained in the DC/FSCCSD calculations. This should be a good approximation for the states studied here, because the dependence of the Gaunt interaction on internuclear separation does not change much upon the addition or removal of an electron or inclusion of electron correlation. Since our basis set is rather small, basis set superposition errors (BSSEs) are non-negligible and need to be corrected for. They were calculated at the FSCCSD level of theory using the counterpoise method and fitted to an exponential form. We calculated 25 potential points in the range of 2.0–4.0 Å. The minimum of each curve was obtained by quadratic fit, using three points spaced 0.005 Å or less around the minimum. Other spectroscopic constants were calculated using the program LEVEL.[24]

TABLE I. Spectroscopic constants of the I_2 molecule. R_e is in Å, D_e in eV, other values in cm^{-1}.

	R_e	ω_e	D_e	$\omega_e x_e$
	$I_2(\sigma_g^2\pi_u^4\pi_g^4)^1\Sigma_{g,0}^+$			
Experiment				
Reference 41	2.666	214.5	1.55	0.614
Present calculations				
DC/FSCCSD	2.691	214	1.47	0.50
DCG/FSCCSD+BSSE	2.711	209	1.32	0.53
Other calculations				
DC/CCSD(T)[a]	2.685	217	1.53	0.58
PP/CCSD(T)[b]	2.668	215	1.57	

[a]Reference 21.
[b]Reference 42.

The spectroscopic constants for the $^1\Sigma_g^+$ ground state of the neutral species (Table I) are in line with previous work.[21] The bond length is found to be about 5 pm too large, which is mainly due to truncation errors in the single particle basis. The calculated constants for the $^2\Sigma_u^+$ ground state of the negative ion (Table II) are in reasonable agreement with the

TABLE II. Spectroscopic constants of the I_2^- ion. Units as in Table I.

	R_e	ω_e	D_e	$\omega_e x_e$
	$I_2^-(\sigma_g^2\pi_u^4\pi_g^4\sigma_u^1)^2\Sigma_{u,1/2}^+$			
Experiment				
Reference 25	3.205 ± 0.005	110 ± 2	1.01	
Present calculations				
DC/FSCCSD	3.20	116	0.91	0.37
DCG/FSCCSD+BSSE	3.24	112	0.82	0.36
Other calculations				
NR/MRCI+SO[a]	3.22	116	1.16	0.36
PP/MRCI+SO[b]	3.22	109	0.98	

[a]Reference 22.
[b]Reference 26.

TABLE III. Spectroscopic constants of the I_2^+ ion. Ionization potentials in eV, other units as in Table I.

	R_e	ω_e	I_e	$\omega_e x_e$
	$I_2^+(\sigma_g^2\pi_u^4\pi_g^3)^2\Pi_{g,3/2}$			
Experiment				
Reference 43		240±1	9.31	0.71
Present calculations				
DC/FSCCSD	2.61	242	9.13	0.67
DCG/FSCCSD+BSSE	2.63	235	9.15	0.64
Other calculations				
PP/SOCI[a]	2.69	217		
DC/CCSD(T)[b]	2.61	238	9.13	
	$I_2^+(\sigma_g^2\pi_u^4\pi_g^3)^2\Pi_{g,1/2}$			
Experiment				
Reference 43		230±2	9.95	0.75
Present calculations				
DC/FSCCSD	2.62	233	9.76	0.71
DCG/FSCCSD+BSSE	2.63	226	9.77	0.69
Other calculations				
PP/SOCI[a]	2.69	208		
DC/CCSD(T)[b]	2.63	227	9.74	
	$I_2^+(\sigma_g^2\pi_u^3\pi_g^4)^2\Pi_{u,3/2}^+$			
Experiment				
Reference 43		138±2	10.71	0.46
Present calculations				
DC/FSCCSD	2.91	158	10.80	0.58
DCG/FSCCSD+BSSE	2.94	152	10.76	0.60
Other calculations				
PP/SOCI[a]	3.09	132		
DC/CCSD(T)[b]	2.95	140	10.97	
	$I_2^+(\sigma_g^2\pi_u^3\pi_g^4)^2\Pi_{u,1/2}^+$			
Experiment				
Reference 45			11.54	
Present calculations				
DC/FSCCSD	2.88	168	11.51	0.51
DCG/FSCCSD+BSSE	2.91	162	11.47	0.49
Other calculations				
PP/SOCI[a]	3.11	112		
DC/CCSD(T)[b]	2.91	156	11.65	
	$I_2^+(\sigma_g^1\pi_u^4\pi_g^4)^2\Sigma_g^+$			
Experiment				
Reference 45			12.66	
Present calculations				
DC/FSCCSD+BSSE	2.97	129	12.57	0.79
DCG/FSCCSD+BSSE	3.01	121	12.52	0.83
Other calculations				
PP/FOCI[a]	3.62	72		

[a]Reference 44.
[b]Referrence 21.

TABLE IV. Spectroscopic constants of the HgH ground state. R_e is in Å, D_e in eV, other values in cm^{-1}.

	R_e	ω_e	D_e	B_e	$\omega_e x_e$
	$HgH(\sigma^2\sigma')^2\Sigma_{1/2}^+$				
Experiment					
Reference 41	[1.766]	[1203]	0.46	[5.39]	
Reference 31	1.741	1385	0.46	5.55	75
Reference 36	1.740	1387	0.46	5.55	83
Reference 29	1.735	1421	0.46	5.59	121
Present calculations					
DC/FSCCSD-1	1.679	1664	0.59	5.84	57
DC/FSCCSD-2	1.703	1555	0.55	5.65	84
DC/FSCCSD-1(+BSSE)	1.721	1552	0.32	5.55	62
DC/FSCCSD-2(+BSSE)	1.750	1423	0.29	5.33	100
DC/FSCCSD-1(+BSSE)+(13eT)	1.753	1359	0.40	5.30	89
DC/FSCCSD-2(+BSSE)+(13eT)	1.758	1361	0.40	5.26	108
Other calculations					
GRECP/FSCCSD(13e-T)-1[a]	1.730	1424	0.41	5.62	81
GRECP/FSCCSD(13e-T)-2[a]	1.738	1362	0.41	5.56	93
RECP/MRD-CI[b]	1.777	1309	0.32		
PP/ACPF+SO[c]	1.722	1414	0.44		

[a]Reference 35.
[b]Reference 34.
[c]Reference 33.

experimental values of Zanni *et al.*[25] The error in the bond length (3–4 pm) is similar to that found for the neutral species, and is ascribed to the same source. Table II also shows the results of multireference configuration interaction (MRCI) calculations[22,26] using larger single-particle basis sets but treating spin–orbit coupling perturbatively. With this method one can also calculate other states of the negative ion that differ by two excitations from the ground state. In the Fock space method these should be calculated using a different reference determinant or using higher sectors of the Fock space. We studied briefly the excited $^2\Pi_{g,1/2}^+$ state observed by Zanni *et al.*[27] who estimated it to be weakly bound with a D_e of 0.02 eV and a bond length of 6.2 Å. This state may be considered to have the configuration $\sigma_g^2\pi_{u,1/2}^2\pi_{u,3/2}^2\pi_{g,1/2}^1\pi_{g,3/2}^2\sigma_u^2$, and the excited configuration $\sigma_g^2\pi_{u,1/2}^2\pi_{u,3/2}^2\pi_{g,3/2}^2\sigma_u^2$ of the neutral molecule was therefore used as reference in this case. The $^2\Pi_{g,1/2}^+$ state then belongs to the $(0h,1p)$ sector of Fock space, and may be calculated without technical problems. The resulting potential energy curve does not show a minimum at this level of theory. Sharp and Gellenne[22] report MRCI calculations with inclusion of spin–orbit coupling and utilizing a large basis with three sets of s,p,d,f,g,h,i polarization functions. Experimental data are well reproduced, indicating that large single-particle expansion sets are needed to get reliable results for this state.

All the low-lying states of the molecular cation are easily calculated in the $(1h,0p)$ sector of Fock space. Calculated spectroscopic constants are collected in Table III and compared with experiment and with previous calculations. The present values are fairly close to the values of de Jong *et al.*[21] obtained by single reference coupled cluster with singles and doubles perturbative triples. The Fock-space method makes possible the calculation of the high-lying $^2\Sigma_{g,1/2}^+$ state, not accessible by the single reference approach. Satisfactory agreement with available experimental data is obtained.

TABLE V. Spectroscopic constants of HgH low excited states.

	R_e	ω_e	T_e	B_e	$\omega_e x_e$
	HgH*$(\sigma^2\pi^1)^2\Pi_{1/2}$				
Experiment					
Reference 41	[1.601]	[1939]		[6.56]	
Reference 36	1.586	2066	24 578	6.68	[64]
Reference 31	1.583	2068	24 590	6.70	65
Reference 30	1.583	2031	24 609	6.71	47
Present calculations					
DC/FSCCSD-1	1.565	2133	23 990	6.78	42
DC/FSCCSD-1(+BSSE)	1.593	2025	23 990	6.50	36
DC/FSCCSD-1(+BSSE)+(13eT)	1.597	1990	24 630	6.46	43
Other calculations					
GRECP/RCC-SD(13e-T)-1[a]	1.582	2065	24 688	6.71	44
RECP/MRD-CI[b]	1.615	2023	25 664		
PP/CASSCF+MRCI+CIPSO[c]	1.603	1946	25 004		
	HgH*$(\sigma^2\pi^1)^2\Pi_{3/2}$				
Experiment					
Reference 31	1.581	2091	28 283	6.73	61
Reference 41	1.579	2068	28 274	6.74	43
Reference 36	1.580	2067	28 256	6.73	42
Present calculations					
DC/FSCCSD-1	1.562	2150	27 480	6.80	42
DC/FSCCSD-1(+BSSE)	1.589	2040	27 480	6.52	34
DC/FSCCSD-1(+BSSE)+(13eT)	1.594	2005	28 122	6.49	40
Other calculations					
GRECP/FSCCSD(13e-T)-1[a]	1.579	2083	28 275	6.74	42
RECP/MRD-CI[34]	1.615	2033	28 490		
PP/CASSCF+MRCI+CIPSO[c]	1.610	1930	28714		

[a]Reference 35.
[b]Reference 34.
[c]Reference 33.

TABLE VI. Spectroscopic constants of the HgH^+ ion.

	R_e	ω_e	D_e	B_e	$\omega_e x_e$
	$HgH^+(\sigma^2)^1\Sigma_0^+$				
Experiment					
Reference 41	1.594	2028	(3.11)	6.61	41
Reference 36	1.594	2034	(2.4)	6.61	46
Present calculations					
DC/FSCCSD-1	1.573	2104	2.57	6.69	42
DC/FSCCSD-1(+BSSE)	1.605	2023	2.57	6.41	32
DC/FSCCSD-1(+BSSE)+(13eT)	1.607	2020	2.55	6.42	33
Other calculations					
GRECP/RCC-SD(13e-T)-1	1.591	2044	2.70	6.64	41
GRECP/RCC-SD(13e-T)-2	1.596	2051	2.59	6.60	32
PP/ACPF[a]	1.593	1959	2.69		

[a]Reference 33.

IV. THE HgH MOLECULE

The HgH molecule has been studied extensively in recent years, both experimentally (see, e.g., Refs. 28–31) and theoretically (Refs. 32–35, among others). There are several reasons for the interest in this molecule. The ground state potential serves as a classical example of rotational predissociation.[29,36] In addition, it possesses a rather deep minimum for a van der Waals type complex; the measured binding energy of 0.3744 eV[29] indicates an intermediate case between a weak chemical bond and pure van der Waals interaction. The formation of a bound state and the large anharmonicity were ascribed by Mulliken[37] to the quasidegenerate nature of the ground state and to strong interaction between the ground nonbonding configuration arising from ground state atoms and the excited bonding configuration of $^2\Sigma^+$ symmetry arising from the Hg($6\,^3P$) and H($1\,^2S$) atomic states.

The goals of the theoretical studies included the interpretation of available experimental data and testing the reliability and accuracy of methods developed for calculations of molecules containing heavy atoms. To our knowledge, all reported calculations of the HgH molecule employed effective core potentials. Among the most sophisticated recent calculations are the relativistic effective core potential multireference double excitation configuration interaction (RECP/MRDCI) work of Alekseyev *et al.*,[34] the pseudopotential averaged coupled pair function plus spin–orbit coupling (PP/ACPF+SO) approach of Häussermann *et al.*,[33] and the recently reported generalized RECP Fock-space relativistic coupled cluster with singles and doubles (GRECP/FSCCSD) scheme of Mosyagin *et al.*[35] Twelve[34] or twenty[33,35] electrons were treated explicitly in these calculations, with the others accounted for by an effective core potential.

Here we report the first all-electron calculation of HgH, carried out in the framework of the Dirac–Coulomb Hamiltonian and including correlation by the FSCCSD method described previously. Two Fock-space schemes were employed. In the first, denoted by DC/FSCCSD-1, the ground state of the HgH^+ ion served as reference. An electron was added in the lowest unoccupied σ or π orbitals to yield the ground and lowest excited states of HgH. The second scheme (DC/FSCCSD-2) started from the ground state of the HgH^- anion as reference and reached the ground state of the neutral molecule by removing an electron from the highest occupied σ orbital. Thirty-five electrons of the HgH molecule were correlated, in order to include core polarization effects. The basis used for the large components included $(20s19p12d10f)/[8s11p6d3f]$ functions on Hg[38] and $(6s3p2d)/[4s3p2d]$ functions on hydrogen.[39] Basis sets for the small components were generated automatically by the MOLFDIR code using the kinetic and atomic balance conditions. Virtual spinors with high orbital energies have been found to contribute very little to correlation effects on molecular properties; spinors higher than 100 a.u. were there-

TABLE VII. Calculated spectroscopic constants of the HgH^- ion.

	R_e	ω_e	D_e	B_e	$\omega_e x_e$
	$HgH^-(\sigma^2\sigma'^2)^1\Sigma_0^+$				
DC/FSRCCSD-1	1.933	894	0.83	4.37	37
DC/FSRCCSD-1(+BSSE)	2.030	776	0.64	3.95	50
DC/FSRCCSD-1(+BSSE)+(13eT)	2.032	824	0.91	3.92	97

fore eliminated from the calculations, effecting considerable saving in computational effort.

The recent two-component GRECP/FSCCSD calculations[35] showed that basis set superposition errors and contributions of virtual triple excitations of the external electrons have considerable effect on HgH spectroscopic constants. These corrections were therefore included in the present work. The BSSEs were estimated by counterpoise correction,[40] and the effect of triple excitations from the outermost 13 electrons of HgH was approximated using the nonrelativistic coupled cluster scheme in the averaged generalized relativistic effective potentials. Details of the latter method may be found in Ref. 35.

Energies of HgH and its ions were calculated at 13 internuclear separations, from 1.3 to 2.5 Å, with intervals of 0.1 Å. Calculated spectroscopic constants of the HgH molecule are shown in Table IV, which also includes results of experiment[29,31,36,41] and previous calculations.[33–35] The $\sigma^2\sigma' X\,^2\Sigma^+$ weakly bound ground state was calculated in both Fock-space schemes, starting from the cation or anion. The singles-and-doubles truncation of the coupled cluster series gives significant differences between the two schemes, indicating sizable contribution of higher excitations. Inclusion of triple excitations from the outermost 13 electrons eliminated the problem, giving very small differences between the two schemes. Good agreement with experiment is obtained when BSSE and triple excitation effects are included.

Spectroscopic constants of the two low excited states of the molecule, arising from the $\sigma^2\sigma' \rightarrow \sigma^2\pi$ excitation, are shown in Table V. Triple excitation effects are smaller in this case, possibly because of the larger spatial separation of σ and π electrons, and CCSD results corrected for BSSEs are in good agreement with experiment. Inclusion of triples does improve this agreement. Similar behavior is exhibited by the HgH^+ cation (Table VI). The cation shows much stronger bonding than the parent molecule. The calculated adiabatic ionization energy is 8.01 eV. Table VII shows calculated values for the HgH^- anion. We are not aware of experimental results for this species. The calculated dissociation energy of the anion is 0.91 eV, and the adiabatic electron affinity of HgH is 1.01 eV. It should be noted that the basis set used may not include enough diffuse functions to assure high accuracy for the anion; this does not affect the results for the cationic or neutral species.

V. CONCLUSIONS

The Fock-space method is a promising tool for studies in which a number of molecular states need to be calculated. It offers a balanced and economical description similar in quality to more costly single reference approaches. The pilot calculations presented here have not yet reached the accuracy that is routinely achieved in atomic calculations, because the single-particle basis sets used were relatively modest. Given the ease of use of the method and the scalability of the implementation toward more powerful computer systems than used in the pilot calculations, we hope to present results for larger systems and in more extensive basis sets in the near future.

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